The Crystal Structure of a Synthetic Ca-Na Sulfate Apatite $Na_6Ca_4(SO_4)_6(OH)_2$

V. Kahlenberg, A. Piotrowski, R.X. Fischer (U. Bremen, Germany), Y. Lee, J.B. Parise, (SUNY, Stony Brook)

Abstract No. kahl6486
Beamline(s): **X3A1**

Ca-Na sulfate apatites with composition $Na_6Ca_4(SO_4)_6(OH)_2$ have been hydrothermally synthesized and characterized by crystal structure analysis. The material can be formally derived from hydroxyl apatite, $Ca_{10}(PO_4)_6(OH)_2$, by a coupled substitution $Ca^{2+} + PO_4^{3-} \rightarrow Na^{+} + SO_4^{2-}$. Preliminary X-ray powder diffraction investigations indeed indicated a close relationship between $Ca_{10}(PO_4)_6(OH)_2$ and $Na_6Ca_4(SO_4)_6(OH)_2$. Due to the small dimensions of the single crystals we decided to perform the structure investigations on the Ca-Na sulfate apatite using synchrotron radiation at beamline X3A1. The basic crystallographic data of $Na_6Ca_4(SO_4)_6(OH)_2$ can be summarized as follows: The compound is hexagonal, space group P -6, a=9.443(1)Å and c=6.886(1)Å. The structure was solved by direct methods. Subsequent refinement calculations converged to a weighted R-value of 0.058 for 1078 reflections with $I > 2\sigma(I)$. The comparison with $Ca_{10}(PO_4)_6(OH)_2$ (space group P 6_3/m) reveals a change in space group symmetry. The symmetry reduction is a consequence of a cation ordering process. The Ca- and Na-cations are not statistically distributed among the two crystallographically different cation positions in the classical apatite space group symmetry P 6_3/m, but order in such a way, that the center of symmetry present in P 6_3/m is lost. The structures of both compounds are compared in **Figure 1**.

Since $Na_6Ca_4(SO_4)_6F_2$ and $Na_6Ca_4(SO_4)_6Cl_2$ crystallize in space group P 6_3/m [1] with disordered cation distributions the ordering process in $Na_6Ca_4(SO_4)_6(OH)_2$ has to attributed the influence of the hydroxyl groups residing on the threefold axis.

Acknowledgments: The authors thank the NSF for financial support (Grant DMR 97-13375). Research carried out in part at the NSLS at BNL is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, Office of Basic Energy Sciences (Grant DE-FG02-86ER45231 for the SUNY X3A beamline).

References: [1] A. Piotrowski, V. Kahlenberg, R.X. Fischer (2000) Z. Kristallogr. Supl. 17, 182.

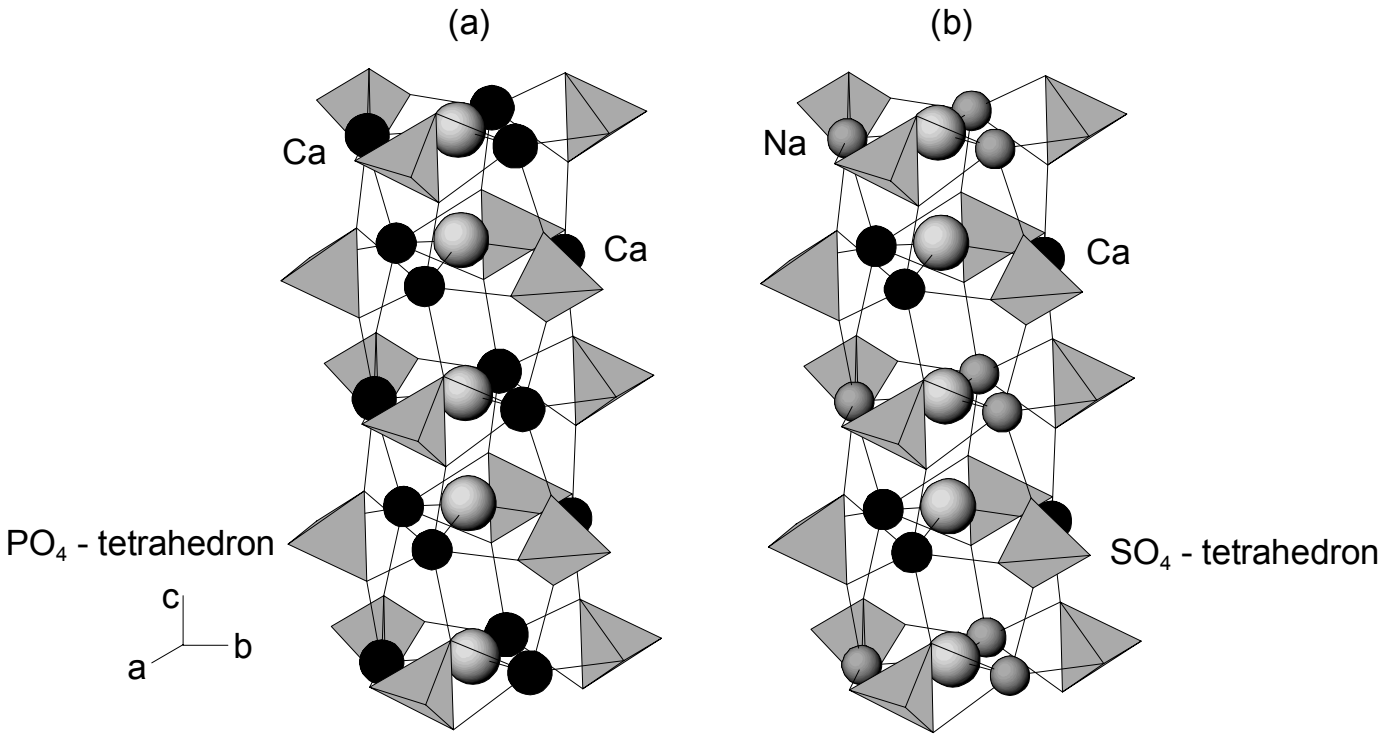

Figure 1: Side view of the crystal structures of (a) $Ca_{10}(PO_4)_6(OH)_2$ and (b) $Na_6Ca_4(SO_4)_6(OH)_2$ The ordering process between the Ca- and the Na-cations inducing the symmetry reduction is shown.